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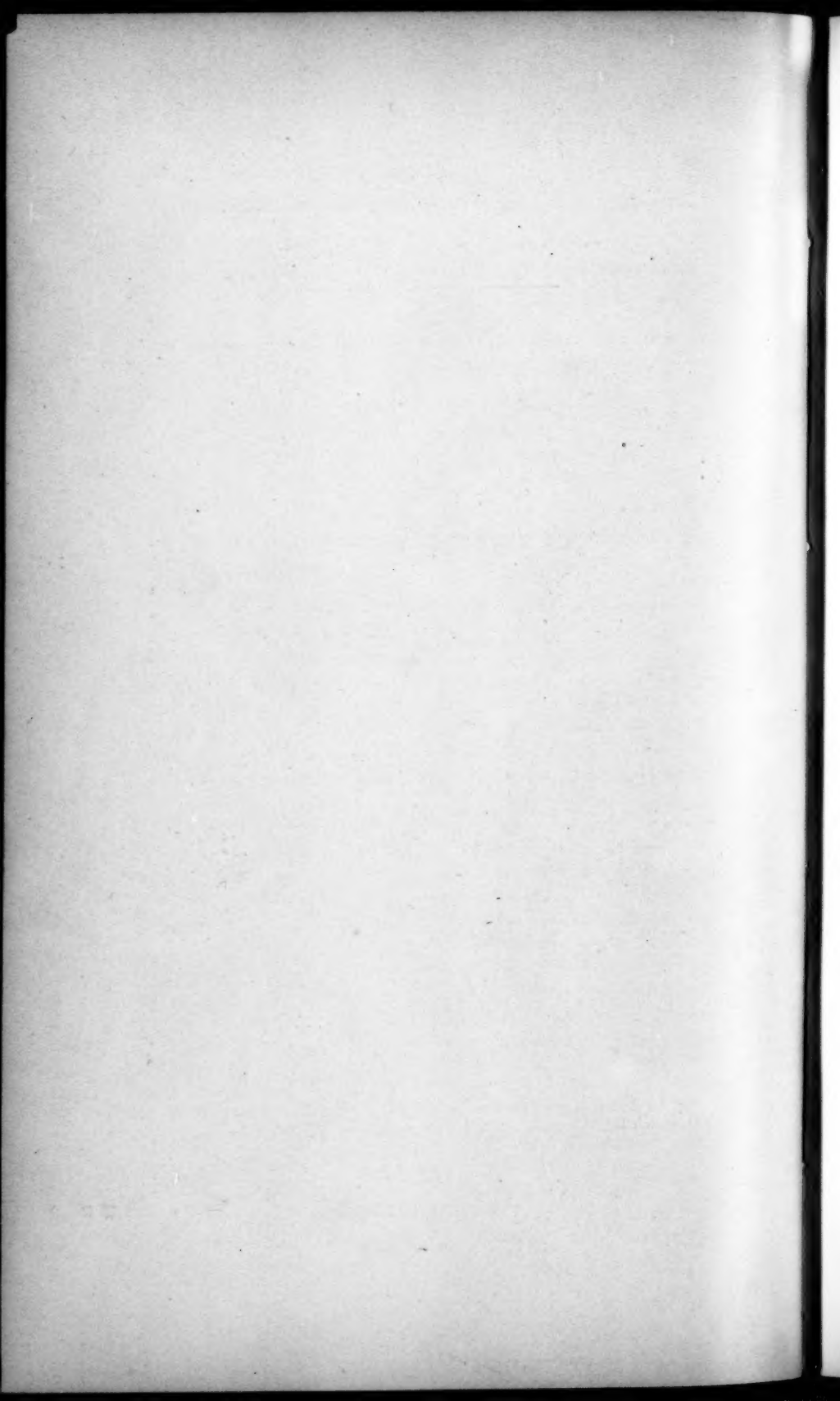
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

*THE TRANSITION TEMPERATURE OF SODIC BROMIDE;
A NEW FIXED POINT IN THERMOMETRY.*

BY THEODORE W. RICHARDS AND ROGER C. WELLS.

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INTRODUCTION.

RECENT work upon the transition temperatures of crystallized salts has shown that many of these transition temperatures are capable of determination with accuracy enough to serve as a means of standardizing thermometers.¹ A number of such points have been found approximately by Richards and Churchill, and one of these points, namely, the transition of sodic sulphate at 32.383° , has been fixed with great precision in reference to the International Scale by Richards and Wells.

It is highly desirable that as many such points as possible should be determined with great precision, because they furnish means of determining temperature intervals dependent only upon the procuring of pure materials, and independent of the possession of a standard thermometer. Among the many transition temperatures to be investigated, two especially promised great usefulness, — one, that of sodic bromide, 50.7° , lying about half-way between the freezing and boiling points of water, and therefore capable of testing the middle of the thermometric scale; and the other, that of sodic chromate, lying at about the ordinary temperature of a laboratory. Of these two points, the former is discussed in the present paper, and the latter will soon be discussed in considerable detail in another paper. Both were determined approximately by Richards and Churchill in the paper already cited, but these determinations were only of a crude and preliminary nature, and required careful verification.

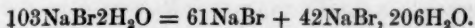
¹ Richards, *Am. Jour. of Science*, **6**, 201 (1898); Richards and Churchill, *These Proceedings*, **34**, 277 (1899); Richards and Wells, *ibid.*, **38**, 431 (1902); also *Zeit. f. phys. Chem.*, **26**, 690 (1898).

It is well known that the presence of impurities affects greatly the transition temperature of a crystallized salt, just as it affects the melting point of a pure substance. Obviously, great purity is demanded if an accurate temperature is to be attained; hence, from the practical point of view, those salts will be most desirable whose purity is most easily attained, other conditions being equal. Thus the turning point of a research upon this subject is the purification of the materials, just as it is in any other accurate chemical investigation. It is therefore necessary that such a research be carried on in a chemical, and not in a physical, laboratory.

As has been said, the ease of purification of the salt chosen is one of the important criteria determining the choice, but this is by no means the only criterion. It is important also that the salt should have as large a heat of transition as possible in order that the accidental addition of outside heat or impurity shall affect the transition temperature as little as possible. Moreover, it is desirable that the salt should not possess the property of forming many hydrates, because there is in this case danger of confusion, and of consequent inexact results. It is also important, although less essential, that the change of volume during the transition should be slight, in order that change of barometric pressure should cause but little difference in the transition temperature. As a rule, however, this last condition is not a very rigorous one, because, even in a case where the change of volume is as much as in melting ice, the changes ordinarily occurring in barometric pressure are barely perceptible on the most accurate thermometers.

From the point of view of the phase rule the transition temperature of a crystallized salt is a quadruple point, involving the coexistence of four phases. As a matter of convenience, however, it is more satisfactory to determine the temperature of another point, almost identical, whose fixity is determined, in the presence of the two components anhydrous salt and water, by the coexistence of three phases, — hydrated salt, dehydrated salt, and solution, under a definite pressure, — that of the atmosphere plus that of the small layer of liquid above the thermometer bulb. These four conditions (three phases and the pressure) are in this case the $n + 2$ conditions which determine invariance in the system composed of the $n = 2$ components. Theoretically, as long as a trace of each of these phases is present the temperature will be constant, but practically it is well to have a fair proportion of each in order to establish the equilibrium as promptly as possible; supercooling or superheating are thus most satisfactorily avoided.

In this case the reaction is a transition from the dihydrate ($\text{NaBr} \cdot 2\text{H}_2\text{O}$) to the anhydrous salt (NaBr) and its saturated solution; the result is to be represented approximately by the following statement:—



This statement is based upon the known fact that a saturated solution of sodic bromide at the transition temperature contains about 116.8 parts of anhydrous salt to 100 of water; in other words, almost exactly 42 grams of anhydrous salt dissolve in the two gram-molecules (36 grams) of water set free from one gram-molecule of salt. The transition is represented upon the accompanying diagram of solubility curves.

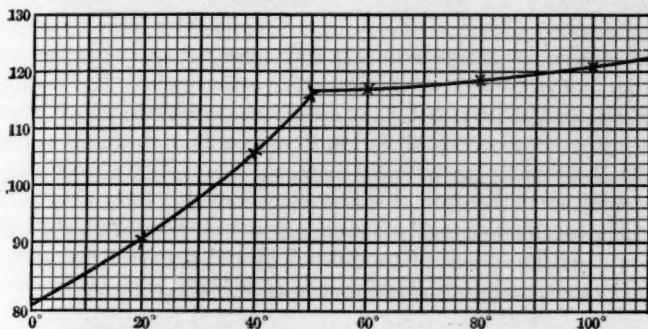


FIGURE 1. SOLUBILITY OF SODIC BROMIDE IN WATER.

The heat of this reaction may easily be computed approximately, although we have not the data for exact computation. Obviously, except for the effect of the possible change of heat capacity of the reacting system during the reaction, the method of calculation is simply to subtract from one another the heats of solution of the initial and final systems in a large excess of water. This would give the hypothetical heat of reaction at 20° , to which a correction would have to be added in order to compute its value at 50° . Now, Thomsen has found that the heat of solution of a gram-molecule of crystallized sodium bromide in water is -4.71 Calories, or -19.7 kilojoules, and that the heat of solution of anhydrous sodium bromide is only -0.19 Calorie, or -0.8 kilojoules. Neglecting the heat of dilution of the part dissolved in transition, we may thus compute the heat of transition to be $-19.7 + \frac{61}{103} \times .8 = 19.2$ kilojoules. It may be of interest to compare this with the latent heats

of melting of corresponding quantities of several single component systems; of water, the latent heat of melting of a gram-molecule is 5.8 kilojoules; and of bromine, 5.4 kilojoules; of iodine, 6.3; of phosphorus, 0.6 for each gram atom. It is apparent from this comparison that, even taking into account the fairly large molecular weight of sodic bromide (139), the heat of transition compares favorably even with the best single component systems.

It becomes now a matter of great interest to calculate as nearly as possible the effect of impurity in the sodic bromide upon the transition temperature. Sodic chloride may be taken as an example, being the most probable impurity. Van't Hoff has pointed out, and Löwenherz² has shown practically, that the transition temperature of a crystallized salt is lowered by the addition of a foreign substance just as a true melting point is lowered. Löwenherz found the molecular lowering to be a constant when the foreign substance added was not an electrolyte, and very nearly a constant in the case of other sodium salts. Undoubtedly the reason for this latter fact is the slight ionization of the added sodium compound in the presence of the large concentration of ionized sodium already dissolved in the saturated solution. Precisely the same conditions apply here; therefore it is safe to assume that sodic chloride, if present in the solution, would act essentially as an undissociated substance. If, now, the phenomenon of transition is viewed simply as the melting of the hydrate, a simple thermodynamic cycle leads to the approximate

equation $\lambda = \frac{n}{N} \frac{RT^2}{\Delta t}$ for the heat of transition of the crystallized salt, in which n and N represent respectively the numbers of moles of impurity and solvent salt, and Δt the change in temperature of transition caused by the admixture, n being supposed to be very small in proportion to N . Substituting the value of λ resulting from the calculation given just above and the molecular weights, it is easy to find that the lowering of the transition point produced by one per cent by weight of this impurity will be about a degree. In other words, the lowering of the transition temperature caused by an impurity of sodic chloride in sodic bromide should be in thousandths of a degree approximately equal to the per cent of impurity expressed in thousandths of a per cent. That is, an impurity of, for example, 0.002 per cent would cause a depression of about 0.002°. This, of course, is only a rough calculation for several reasons. In the first place, the temperature of transition is 50.7°, not

² Zeit. phys. Chem., 18, 70 (1895).

20°, to which the reaction heat corresponds. In the next place, the transition is not a simple melting, although, indeed, it is true that the equation of van't Hoff applies as a close approximation. It is not, however, worth while to attempt a closer calculation of these quantities for the reason that further elaborate experimentation would be required in order to demonstrate the disposition of the sodic chloride in this mixture. It is not known whether or not the salts are isomorphously mixed in both solid phases, — a circumstance presenting a series of complications quite untraceable on the basis of data known at present. However, the above calculation probably shows the maximum effect to be produced by a substance with even as low a molecular weight as 58.5. Of course, substances with higher molecular weights would produce proportionately smaller effects for a given percentage composition, and therefore be even less objectionable for the present purpose. Practically we found that sodic bromide containing about .02 per cent of sodic chloride actually "melted" at a temperature only about 0.013 or 0.014 too low.

It is worth while now to compare the effect of impurity in sodic bromide with the effect of impurity in water. The lowering caused by a gram molecule of non-electrolyte in a litre of water is 1.86°, therefore an impurity of .01 per cent of the electrolyte common salt would cause a change of 0.006°. This is a somewhat smaller effect of impurity than in the case of the sodic bromide; the comparison emphasizes strongly the importance of purity in the materials in the latter case.

PREPARATION OF SODIC BROMIDE.

The preparation of pure sodic bromide proved to be unexpectedly difficult, but the difficulties have been surmounted, and the result of the present work must be considered as essentially final. The problem is harder than that involving sodic sulphate, and we cannot recommend sodic bromide with quite the unqualified approval which the other salt received; nevertheless, although not so easy to repeat, the preparation is by no means impossible, and the results will certainly serve a useful practical purpose.

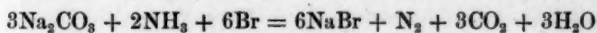
At first it was attempted to purify the two different specimens of commercial bromide by recrystallization as dihydrate with the hope that the chloride would be thus easily eliminated, because of the very low inversion temperature of the corresponding sodium salt. However, the result in each case was very disappointing. The bromide, although increasing in purity with each successive crystallization as shown by

the steadily rising transition temperature, did not lose its impurity fast enough to make any considerable final yield a possibility. The commercial salt sometimes gives results several degrees in error, and even after eight recrystallizations one sample melted over half a degree below the true point. Such material is of course wholly out of the question. Perhaps some other isomorphous impurity beside sodic chloride was present. Whatever may have been the cause of the trouble, this crude material was entirely rejected in subsequent work, and all other samples were made from pure hydrobromic acid or bromine and pure alkali.

The next preparation of sodic bromide was made from purified sodic carbonate and hydrobromic acid. The sodic carbonate was five times recrystallized, and the bromine, from which the hydrobromic acid was made, was freed from chlorine by solution in calcic bromide and reprecipitation by water. The bromine was converted into hydrobromic acid with the help of carefully washed red phosphorus and water. Hydrobromic acid, prepared in this way, contains phosphorus and sometimes traces of arsenic; but three successive fractional distillations easily removed these impurities. The purity of the product and the residue was determined in each case by ammonium molybdate. The first residue, after the distillation of about eight kilograms of fifty per cent hydrobromic acid in the retort, yielded about thirty grams of ignited phosphomolybdenum oxide. The residue from the second distillation yielded only a quarter of a gram, and the residue from the third distillation gave no precipitate whatever with the ammonic molybdate. The distillate was of course even more pure than this, because the impurities concentrate in the residue. Iodine was expelled in the first aqueous fractions by adding bromine water before each distillation. No attempt was made to eliminate the iodine by adding zinc oxide according to Stas, because this method seemed to us of doubtful efficacy. As will be shown later, the sodic bromide (sample II) prepared thus was very pure, but it had not yet attained the greatest purity possible, because the single treatment with calcic bromide is usually insufficient to remove every trace of chlorine from the commercial bromine. A number of other samples were made in this way, and according to the amount of chlorine in the original crude bromine, the substance obtained varied from a state of almost perfect purity to a state of contamination with 0.05 per cent of its weight of sodic chloride. Protracted and tedious quantitative precipitations of silver bromide, conducted with all the accuracy of atomic weight determinations, were necessary to prove this fact and explain slight irregularities in the transition temperatures

of the several specimens of the various samples. These analyses need not be detailed here, because all of the specimens used in the final work to be recounted were as free as possible from chlorine, but they were amply worth the trouble which they occasioned, because they not only proved the slight impurity in the bromine, but also led to the subsequently confirmed suspicion concerning the atomic weights of sodium and chlorine.

The reason for this difficulty in preparing pure bromine is clear. The elimination of chlorine from bromine by solution in calcic bromide and precipitation with water is a question of the distribution of the chlorine between two phases, much the greater part of the chlorine going into the aqueous phase. When the amount of the chlorine in the original bromine is small, a good product may be obtained by a single treatment; but when it is large, several successive treatments must be used in order to eliminate every weighable trace of chlorine. One of the portions of sodic bromide used in the transition temperature work was made from bromine thus purified several successive times in addition to repeated distillation.³ This sample, perhaps as pure as may be obtained by any method, is called III in the work which follows. A fourth (called IV) was prepared by another method of procedure. Potassic permanganate was recrystallized until free from chloride, the tests being made in small portions after precipitation with alcohol and filtration of the manganese dioxide. Sulphuric acid was boiled until free from chloride. With the help of these two substances, bromine was set free from a large sample of pure sodic bromide (sample II). After shaking with a solution of the bromide, the bromine was twice redistilled. This very pure preparation was run into carefully purified ammoniacal sodic carbonate in a hard glass dish (for platinum might have been slightly attacked) and the solution of sodic bromide was transferred to platinum as soon as the operation was completed. The ammonia used in this process had been prepared from ammonic sulphate purified by treatment with nitric and sulphuric acids in the manner recommended by Scott⁴ to free it from amines. It was twice further distilled into pure water. The reaction may be expressed as follows:



³ This sample had been prepared by T. W. Richards for work on atomic weights.

⁴ Journ. Chem. Soc., 79, 147 (1901).

The sodic carbonate was maintained in slight excess, and this excess finally neutralized by some of the pure hydrobromic acid described above. The salt was recrystallized twice with thorough draining. Very pure material may be made in this way, if the ammonia, bromine, and sodic carbonate are all pure.

The hydrobromic acid used for the fifth and last sample of sodic bromide was made by bubbling electrolytic hydrogen through bromine, and passing the mixture through a hot hard glass tube. The bromine used was in the first place purified by distillation from a bromide, and a further attempt was made to purify it by passing the vapor when mixed with hydrogen before heating over a counter current of a solution of a pure bromide (made from a portion of the acid itself) flowing over beads in tall glass columns. All the apparatus was constructed of glass, without rubber connections, and the current was run slowly; but it is doubtful if great gain was effected by contact with the solution. The reason for the slow purification of a vapor by this means is undoubtedly the fact that the reaction can take place only on the limited surface between the gaseous and liquid phase.⁵

A large quantity of acid thus prepared was neutralized by a new specimen of sodic bicarbonate even purer than before. The bicarbonate was made by precipitating a solution of pure often recrystallized sodic carbonate in platinum through the long continued action of carbon dioxide. The easiest method consists in placing the open dish under a bell-jar and keeping the latter full of the gas at a pressure slightly greater than that of the atmosphere. The carbon dioxide was generated by heating pure dry sodic bicarbonate in a large bomb-shaped vessel, and washed once with a dilute solution of the same salt. The sodic bromide thus prepared served for the last two final determinations given below, after having been recrystallized three times.

In order to remove all doubt as to the purity of salt, a sample prepared in this way was analyzed by the precipitation of argentic bromide with all the precautions of an atomic weight determination, and the result was compared with a similar analysis of a sample made with hydrobromic acid known to be pure. The latter was kindly given by Professor Baxter and Mr. H. L. Frevert, having been made by them

⁵ As a matter of fact, one sample of acid prepared in this way was found by Professor Baxter, who kindly interested himself in the matter, to contain appreciable traces of chlorine. Evidence is given later showing that the particular sample V of sodic bromide prepared from acid thus made was free from this impurity, however.

for the determination of the atomic weight of cadmium. Both specimens of sodic bromide were well drained, desiccated in vacuum, fused in nitrogen, weighed and analyzed by conversion into silver bromide as usual.

Of our sodic bromide 5.49797 grams yielded 10.03253 grams of argentic bromide, and of the other sample 3.64559 grams yielded 6.65248 grams, all the weighings being reduced to the vacuum standard. The respective weights of argentic bromide corresponding to 1.00000 parts of sodic bromide are 1.82477 and 1.82480, showing the essential identity of the samples.

These two analyses not only serve this purpose, however; they likewise furnish new data for calculating the atomic weight of sodium, which is thus found to be 23.008, if silver is taken as 107.930 and bromine as 79.955. The new result from the chloride is also 23.008, an exactly identical figure. Thus the comparison of the results furnishes another reason for believing that the salt used in our transition temperature experiments was pure. Only their small number and our uncertainty concerning the exact atomic weight of bromine debars us from presenting these results in a special paper as a contribution to the literature on atomic weights.

METHOD OF DETERMINING THE TRANSITION TEMPERATURE.

The apparatus necessary for this work naturally divides itself into two parts, — the thermometers on the one hand, and the apparatus for containing the salt on the other. The thermometers employed have all three been standardized with the greatest care by the International Bureau of Weights and Measures in Sèvres. They have already been described in detail in the previous papers.⁶ They were those bearing the designations Tonnelot 11142 and Baudin 15200 and 15275. Further description of them is unnecessary here.

To contain the salt two different arrangements were used. In one case the salt was contained in a wide test-tube placed in the bottom of a long still wider sealed tube sunk in a very deep thermostat until the 50° mark on the thermometer stem was almost level with the water. The object of this device was obviously to maintain the thermometer stem all at the transition temperature in order to avoid any considerable correction for the cooled column.

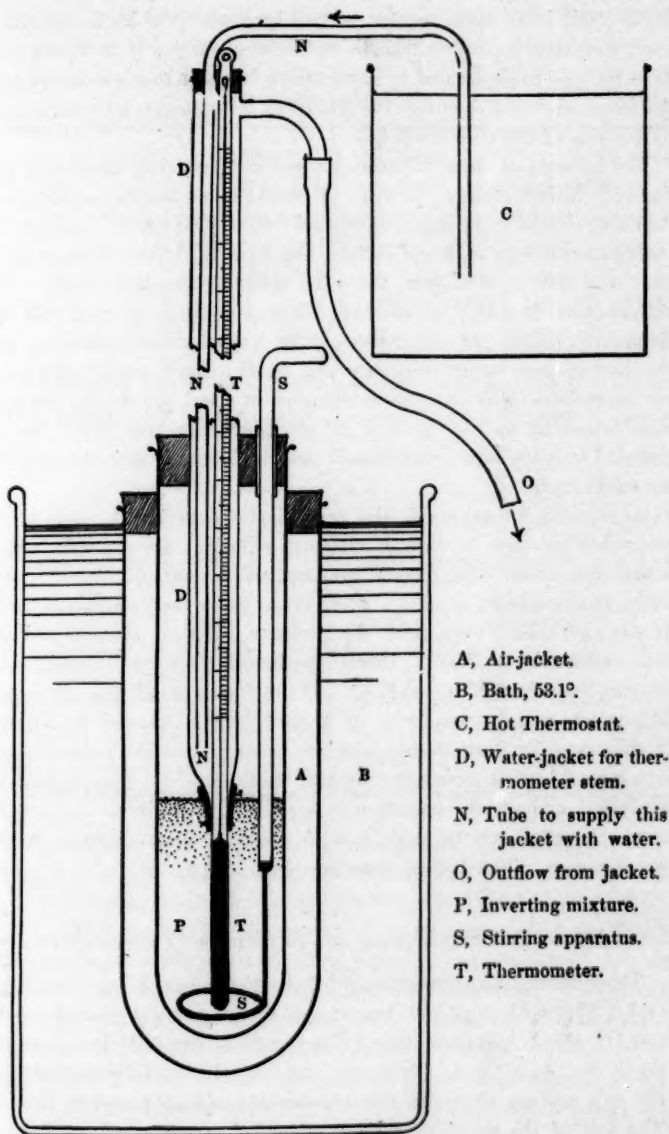
The more convenient apparatus employed in all the other determina-

⁶ Am. Jour. Science, 6, 201 (1898); These Proceedings, 38, 434 (1902).

tions was modelled after that described in the paper upon the sulphate, and is illustrated in the accompanying Figure 2. The tube containing the inverting mixture was surrounded by an air-jacket (A), and the latter by water maintained at the desired temperature above the transition temperature by an electrically heated resistance wire. The thermometer itself was surrounded by a long jacket (D) of good glass through which a current of pure water was maintained, flowing from a large thermostat, in order to keep the stem of the thermometer at the same temperature as the bulb. Preceding experience had taught us to heed the cooling of this stream of water as it flowed from an elevated thermostat (C); of course, at the temperature of 50° , the cooling was even more marked than in the case of sodic sulphate at 32° . To avoid any error on this account, a small extra thermometer was inserted in the long jacket around the standard thermometer to record the temperature of its stem. This extra thermometer is not shown in the diagram. In order to be certain of the temperature of the transition to a thousandth of a degree, it is necessary to be certain of that of the stem to a tenth of a degree. The evenly distributed cooling of the flowing column in the distance represented by the length of the mercury thread amounted to no more than 0.4° , therefore the temperature of the water in the jacket observed at about the middle point of the column could be taken as the average temperature of the column. The thermostat (C) was accordingly set so that the temperature of the flowing water at this point was within a tenth of a degree of the temperature of the inverting salt. In this way the conditions for accurate thermometry were adequately obtained and all uncertain corrections were avoided.

According to the degree of the exposure of the top of the large test-tube containing the mixture it is necessary to maintain the water bath outside its air-jacket at a temperature somewhat above that of the mixture, in order to allow for the cooling effect of convection in the air-jacket. For the particular apparatus employed in these experiments and at the temperature of 50° this interval was found to be 2.5° . With this interval the inflow of heat was so nicely regulated that the temperature of the sodic bromide was maintained for at least two hours with wonderful constancy.

The stirrer used in stirring the salt and solution during the observation of the transition temperature was made of glass and a large sealed-in platinum wire. Platinum alone was first tried, but it was deemed to have too large a thermal conduction; and as the containing tube was glass, a further stirrer of glass could be accepted. Instead of powder-



- A, Air-jacket.
- B, Bath, 53.1°.
- C, Hot Thermostat.
- D, Water-jacket for thermometer stem.
- N, Tube to supply this jacket with water.
- O, Outflow from jacket.
- P, Inverting mixture.
- S, Stirring apparatus.
- T, Thermometer.

FIGURE 2. APPARATUS EMPLOYED.

ing the salt in an agate mortar, as had been our practice in the case of sodic sulphate, we crystallized it by rapid cooling. It is necessary to have the salt finely divided by some means in order to stir it successfully. As far as we could discover, the transition temperature was not affected by the size of the solid crystals.

The ice used in these experiments was a commercial ice of very good purity. Before crushing it was well washed, and thereupon introduced into very carefully purified, boiled, and fully cooled water. Under these circumstances very little ice melted, and accordingly the water around it was very pure. Moreover, the total residue proceeding from a very considerable quantity of this ice alone amounted to only one ten-thousandth of one per cent. Even if the impurity had consisted of sodic chloride or some other substance this small amount could have caused no appreciable effect on the freezing-point; and practically we found that according to this method of procedure the commercial ice surrounded by pure water gave results exactly identical with the purest ice we could make.

As was to be expected, the preliminary experiments gave results somewhat too low, because of traces of chloride; for example, salt II, when crystallized once, gave a transition temperature of 50.661° ; when twice recrystallized, 50.670° ; when three times recrystallized, 50.671° . It was now almost pure, since the probable value of the true transition temperature is 50.674° . Other specimens gave preliminary values ranging from 50.663° to 50.673° . On the other hand, the salt labelled III, which was known to be of greater purity, showed no difference in the transition temperature between the first and the seventh successive crystallization, giving the constant value 50.674 . Having thus both analytical and physico-chemical evidence of the purity of our material, it was therefore safe to make a final series of determinations with all possible care. The data of these are given below.

FINAL DETERMINATIONS OF TRANSITION TEMPERATURE.

Three thermometers were used for the final work, as has already been said. The work with the Tonnelot thermometer was carried out with salt III, which had been recrystallized seven times. It is a pleasure to thank Mr. J. B. Churchill for his assistance in carefully recrystallizing the salt and in aiding in the temperature measurement in this case. The data of the measurement are given below. The salt used for the determinations made with the two Bandin thermometers was that

labelled V, recrystallized three times. The temperature measurements are recorded in the usual fashion, and need no further interpretation.

FINAL MEASUREMENTS.

Thermometer.	Tonnelot. 11142.		Baudin. 15275.		Baudin. 15200.	
	In salt.	In ice.	In salt.	In ice.	In salt.	In ice.
Reading	50.647	+0.098	50.873	0.059	50.719	+0.080
Cor. calibration	+0.159	0.000	-0.059	0.000	+0.064	0.001
" int. pressure	+0.063	+0.016	+0.036	+0.013	+0.055	+0.009
" ext. pressure	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
" exposed column	+0.005	0.000	0.000	0.000	0.000	0.000
" exact 0° point	+50.873	+0.113	50.849	+0.071	50.837	+0.098
	-0.113	←	-0.071	←	-0.098	←
" fundamental interval }	50.760		50.778		50.739	
	+0.016		-0.001		+0.036	
	-0.102		-0.102		-0.102	
" to hydrogen	50.674		50.675		50.673	

Thus, the three final determinations, made with three different thermometers from two makers, and with two different specimens of salt, at widely different times, gave as results respectively, 50.674°, 50.675°, 50.673°. The remarkable agreement of these results must be partly accidental, because the extreme divergence is less than the possible divergence from accuracy of each single determination. The mean, 50.674°, may be taken as representing very nearly the true transition temperature of the salt, on the international hydrogen scale.

In conclusion, it is a pleasure to acknowledge our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for pecuniary aid in carrying on this investigation.

SUMMARY.

The results of this paper may be summed up in the following sentences :

1. Pure sodic bromide is not to be obtained by recrystallizing the ordinary commercial samples, but must be made from pure bromine and pure sodic carbonate.

2. Prepared in this way, our salt upon analysis was found to correspond very closely with the new value of the atomic weight of sodium, 23.008, if silver be taken as 107.93 and bromine 79.955. Therefore, it was presumably pure.

3. The less pure material on successive recrystallization gave in every case a slightly rising transition temperature as the crystallization proceeded. Only the purest material melted at a perfectly constant point, therefore constancy of melting point is an indicator of purity ; but it is safer to analyze the salt as well.

4. When all precautions are taken it is possible to duplicate the results for the transition temperature with samples of salt prepared in different ways and at different times without great difficulty ; a value within $.01^{\circ}$ of the truth may be easily obtained, and further precautions enable one to approach much closer. Therefore, the point is one suitable to use in the calibration of thermometers, although its determination requires more chemical skill than that involving sodic sulphate.

5. The actual value of the transition temperature on the international hydrogen scale is 50.674° .